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**(71)** Applicant: **KONICA CORPORATION**  
**No. 26-2, Nishi-Shinjuku 1-chome**  
**Shinjuku-ku**  
**Tokyo 106(JP)**

**(72)** Inventor: **Mochizuki, Yoshiharu**  
**c/o Konica Corporation 1, Sakuramachi**  
**Hino-shi Tokyo(JP)**  
Inventor: **Ishikawa, Sadayasu**  
**c/o Konica Corporation 1, Sakuramachi**  
**Hino-shi Tokyo(JP)**  
Inventor: **Yagi, Toshihiko**  
**c/o Konica Corporation 1, Sakuramachi**  
**Hino-shi Tokyo(JP)**  
Inventor: **Inoue, Masamitsu**  
**c/o Konica Corporation 1, Sakuramachi**  
**Hino-shi Tokyo(JP)**

**(74)** Representative: **Wood, Anthony Charles et al**  
**Urquhart-Dykes & Lord 91 Wimpole Street**  
**London W1M 8AH(GB)**

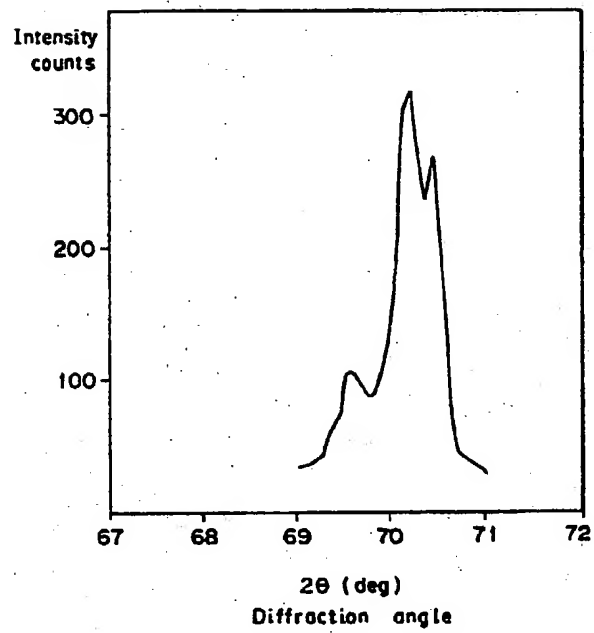
**(54)** High sensitivity, high graininess light-sensitive silver halide photographic material.

**(57)** A light-sensitive silver halide photographic material having at least one layer of emulsion layer containing an emulsion which is a silver halide emulsion containing silver iodobromide grains having 3 or more phases of silver bromide or silver iodobromide with different compositions, the emulsion having, in the diffraction signal according to powdery X-ray diffraction, 3 or more diffraction maximums based on the diffraction peak corresponding to the maximum iodine content phase, the diffraction peak corresponding to the minimum iodine content phase and one or plural number of diffraction peaks corresponding to the intermediate iodine content phase comprising intermediate compositions between the maximum iodine content phase and the minimum iodine content phase, and two or more diffraction minimums therebetween.

According to the present invention, there can be obtained a light-sensitive silver halide photographic material with high sensitivity and high graininess.

**EP 0 309 119 A2**

FIG. 1



## High sensitivity, high graininess light-sensitive silver halide photographic material

BACKGROUND OF THE INVENTION

This invention relates to a light-sensitive silver halide photographic material, more particularly to a light-sensitive silver halide photographic material having high sensitivity and improved graininess.

It has been increasingly demanded to improve image quality for light-sensitive silver halide photographic material. Particularly, practical application of a high sensitivity film of ISO 1000 or higher in the field of color negative film and prevalence of a compact camera of small format as represented by disc film have brought about enlargement of photographing chances, but on the other hand, invited lowering in image quality of print, of which improvement has been desired. Particularly, concerning graininess which is an important factor determining the quality of color photographic image, many studies have been done primarily about silver halide emulsions.

Already, a silver iodobromide emulsion containing 5 mol% or more of silver iodide has been known as the silver halide emulsion having high sensitivity and excellent graininess. Further, as the improved silver iodobromide emulsion, the core/shell type silver halide emulsion containing 5 mol% or more of silver iodide has been abundantly studied. Particularly, for use in color negative films, much studies have been done about silver iodobromide emulsions of the core/shell type with a high silver iodide content phase containing 10 mol % or more of silver iodide in an inner part.

Japanese Unexamined Patent Publication No. 245151/1986 discloses the core/shell type emulsion improved in graininess, and Japanese Unexamined Patent Publications Nos. 143331/1985, 147727/1985 and 254032/1985 disclose the core/shell type emulsions with high silver iodide content.

However, these emulsions proved to be still insufficient in sensitivity and graininess.

The present inventors have examined in detail about the causes for these, and consequently found that the cause for the former is that uniformization of high iodine content phase and low iodine content phase can easily occur during preparation of the core/shell type emulsion having a core with high content of silver iodide, whereby there is involved the drawback that silver halide grains with indistinct phase structure are formed. Also, as to the latter, although separation between high iodine content phase and low iodine content phase may be distinct, they were found to be silver halide grains having separation of substantially two different iodine phases.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a light-sensitive silver halide photographic material having high sensitivity and high graininess.

The present inventors have studied intensively, and consequently found that the object of the present invention can be accomplished by a light-sensitive silver halide photographic material having at least one layer of emulsion layer containing an emulsion which is a silver halide emulsion containing silver iodobromide grains having 3 or more phases of silver bromide or silver iodobromide with different compositions, said emulsion having, in the diffraction signal according to powdery X-ray diffraction, 3 or more diffraction maximums based on the diffraction peak corresponding to the maximum iodine content phase (hereinafter abbreviated as maximum iodine phase), the diffraction peak corresponding to the minimum iodine content phase (hereinafter abbreviated as minimum iodine phase) and one or plural number of diffraction peaks corresponding to the intermediate iodine content phase (hereinafter abbreviated as intermediate iodine phase) comprising intermediate compositions between said maximum iodine phase and said minimum iodine phase, and two or more diffraction minimums therebetween.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 represents a X-ray diffraction pattern of emulsion grains, with the axis of abscissa showing diffraction angle ( $2\theta$ ) and the axis of ordinate diffraction intensity.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention, at least one layer of the silver halide emulsion layers contains the silver iodobromide emulsion of the present invention.

In the method for measuring powdery X-ray diffraction image, for example, synchrotron orbit radiation from the storage ring described in "New Experimental Chemistry Course, Basic Technology 5, Structural Analysis" (Maruzen, 1977), p.81, which is made monochromatic by the monochromator using a single crystal described in the same literature on pages 83 - 84, can be used as the X-ray light source.

In the measurement of the present invention, the half value width obtained when the powdery X-ray diffraction of silicon (111) was measured with the use of X-ray having a wavelength of 1.4908 Å obtained by diffracting twice the synchrotron orbit radiation with a curved silicon single crystal (111) was found to be 0.043° (2θ).

Specific examples of the X-ray diffraction method utilizing synchrotron orbit radiation can be seen in Photon Factory Activity Report, Vol. 3, p.105 (1985). Also, the X-ray monochromator using a single crystal is described in more detail in International Tables For X-ray Crystallography, Vol. 3, P.79 - 86.

In the silver halide emulsion in the present invention, the diffraction signal corresponding to the diffraction line (420) of silver iodobromide has 3 or more of diffraction maximums as the total of the diffraction peak corresponding to the maximum iodine phase, the diffraction peak corresponding to the minimum iodine phase and one or a plural number of diffraction peaks corresponding to the iodine phase comprising intermediate compositions between said maximum iodine phase and said minimum iodine phase, and two or more diffraction minimums therebetween. It is preferable that diffraction intensity corresponding to the phase which gives the highest intensity among the diffraction maximums should be 1 to 50 times, more preferably 1 to 20 times, particularly 1 to 10 times, relative to the diffraction intensity corresponding to the phase which gives the lowest intensity among the diffraction maximums.

As the emulsion having a clear phase structure of 3 or more phases in the present invention, one with the diffraction intensity of the minimum value sandwiched between any adjacent two diffraction maximums being 95 % or less of the weaker one of the adjacent two diffraction maximums (peaks) is preferred. Further preferably, it is 90 % or less.

The noise of the device will not be counted.

The phase structure of 3 or more phases of silver bromide or silver iodobromide in the present invention can be judged by the method of X-ray diffraction. Examples of application of X-ray diffraction method to silver halide grains are described in the literature of H. Hirsch, Journal of Photographic Science, Vol. 10 (1962), P.129 et seq. etc. When lattice constants are determined depending on the halogenic composition, peaks of diffraction occur at diffraction angles which satisfy the condition of Bragg ( $2d\sin\theta = n\lambda$ ).

Even in the case of an emulsion where many kinds of grains with different halogenic compositions comprising respectively uniform phases co-exist, a plural number of peaks may sometimes appear in the above X-ray diffraction.

In such emulsion, no excellent photographic performance obtainable in the present invention can be obtained.

As other method than the X-ray diffraction method, EPMA method (Electron-Probe Micro Analyzer method) also renders possible the judgement whether the silver halide emulsion is the emulsion according to the present invention or an emulsion as mentioned above wherein many kinds of silver halide grains co-exist.

This method can perform elemental analysis of extremely fine portion by X-ray analysis by electron beam excitation in which a sample comprising emulsion grains well dispersed so as to be not contacted with each other is prepared and irradiated with electron beam.

According to this method, by determining the characteristic X-ray intensity of silver and iodine radiated from the respective grains, the halogenic compositions of the individual grains can be determined.

By confirming the halogenic compositions for at least 50 grains by the EPMA method, it can be easily judged whether the emulsion is the emulsion according to the present invention or not.

The emulsion of the present invention should preferably contain grains having more uniform iodine contents therebetween. When the distribution of iodine contents between the grains is measured by the EMPA method, the relative standard deviation should be 50 % or less, preferably 35 % or less, particularly 20 % or less.

Preferable halogenic compositions of the silver halide grains having the phase structure of 3 or more phases of the present invention are as described below.

The silver iodobromide emulsion of the present invention is a grain composed of the maximum iodine phase, the minimum iodine phase and the intermediate iodine phase therebetween, the intermediate being formed of one or more phases. The silver iodide contents in the maximum iodine phase, the minimum iodine phase and the intermediate iodine phase therebetween differ from each other.

5 The silver iodide content in the maximum iodine phase should be preferably 10 mole% or more, more preferably 15 to 45 mol %, particularly 20 to 40 mol%. The silver iodide content in the minimum iodine phase should be preferably 6 mole% or less, more preferably 0 to 3 mole%. The percentage of the minimum iodine phase in the silver halide grains of the present invention should be preferably 10 to 80 % by volume, more preferably 15 to 70 %, particularly 20 to 60 %.

10 The percentage of the maximum iodine phase in the whole grains should be desirably 10 to 80 % by volume, more preferably 20 to 50 %.

The silver iodide content in the intermediate iodine phase should be preferably 3 mole% or more, respectively, further preferably 5 mole% or more, respectively, when it is represented in terms of the difference in silver iodide content between the maximum iodine phase and the intermediate iodine phase or 15 between the intermediate iodine phase and the minimum iodine phase.

The preferable percentage of the intermediate iodine phase in the whole grains should be preferably 5 to 60 %, more preferably 20 to 50 %.

The silver halide grains of the present invention may comprise either normal crystals such as cubic, tetradecahedral, octahedral crystals, twin crystals or mixtures thereof, but preferably normal crystals.

20 In the silver halide grains of the present invention, the maximum iodine phase may exist anywhere within the grain, but preferably as the internal nucleus (core) internally of the grain. Also, although the minimum iodine phase may exist anywhere within the grain, but it should preferably exist as the shell outside of the internal nucleus. One or a plural number of intermediate iodine phases may also exist anywhere within the grain, but should preferably exist as the intermediate layer between the internal nucleus and the shell, also preferably exist inside of the internal nucleus, or can also exist in both thereof.

25 The silver halide emulsion of the present invention is a silver iodobromide, preferably with an average silver iodide content of 5 mol% or more, more preferably 6 to 15 mol%. Also, silver chloride can be contained within the range which does not impair the effect of the present invention.

30 The silver halide grains according to the present invention should be preferably the core/shell type emulsion, and as the preparation method thereof, those disclosed in Japanese Unexamined Patent Publications Nos. 177535/1984, 138538/1985, 52238/1984, 143331/1985, 35726/1985, 258536/1985 and 245151/1986 can be used. That is, it is possible to use a method in which the seed emulsion is grown according to the double jet method, while controlling pAg and pH.

35 In preparation of the silver halide emulsion of the present invention, control of pAg during preparation is very important. The pAg during growth of core should be preferably 6 to 10, while the pAg during growth of shell may be preferably 9 to 11.

The pAg change during formation between the core and the shell may be varied either stepwise or continuously, but preferably continuously.

40 In preparation of the silver halide emulsion of the present invention, the feeding method, stirring method or stirring condition during preparation is very important. Namely, feeding of the reaction solutions should be preferably performed by a feeding method characterized by the following:

A plurality of feeding nozzles are provided for one reaction solution in such a manner that said feeding nozzles are immersed in the mother liquid in reaction tank and located adjacent to the mother liquid inlet of the stirrer provided in the tank, so as to give a homogeneous mixed solution in a shorter period.

45 More specifically, as the feeding device or the stirring device, the device as shown in Japanese Unexamined Patent Publication No. 160128/1987 may be preferably employed at a rotational number of 500 to 1200 rpm.

50 When the core/shell type silver halide emulsion is grown starting from the seed emulsion as in the method disclosed in Japanese Patent Publication No. 138538/1985, it can have a silver halide composition region different from that of core at the central portion of the grain. In such case, the halogenic composition of the seed grain may be any desired composition of silver bromide, silver iodobromide, silver chloriodobromide, silver chlorobromide, silver chloride, etc., but preferably silver iodobromide with a silver iodide content of 10 mole% or less or silver bromide.

55 The ratio of the seed grain occupied in the whole silver halide may be preferably 50 % or less in volume, particularly 10 % or less.

During growth of silver halide grains, known solvents for silver halide such as ammonia, thioether, thiourea, etc. can be permitted to exist.

Silver halide grains can be added with at least one metal ion selected from cadmium salts, zinc salts,

lead salts, thallium salts, iridium salts (including complexes), rhodium salts (including complexes) and iron salts (including complexes) to incorporate these metal atoms internally of the grains and/or in the surface layers of the grains, and can be also placed in a reducing atmosphere to impart reduced sensitizing nuclei into the grains or onto the grain surfaces.

The silver halide emulsion may have unnecessary soluble salts removed or contained as such after completion of the growth of silver halide grains. When said salts are to be removed, removal can be practiced on the basis of the method described in Research Disclosure (hereinafter abbreviated as RD) No. 17643, Item II.

The silver halide grain may be any of the grain in which latent image is formed primarily on the surface or primarily internally of the grain, and the size of the silver halide grain may be 0.05 to 30  $\mu\text{m}$ , preferably 0.1 to 20  $\mu\text{m}$ .

As the silver halide emulsion in the present invention, any of poly-dispersed emulsions with broad grain size distribution and mono-dispersed emulsions with narrow grain size distribution can be used. In practicing the present invention, it is preferable to use a mono-dispersed emulsion alone or as a mixture after sensitization.

In the present invention, the mono-dispersed silver halide emulsion may be preferably one in which the weight of silver halide grains having a grain size included within the range of  $\pm 20\%$  from an average grain size  $\bar{r}$  as the center corresponds to 60 % or more of the weight of all the silver halide grains, more preferably 70 % or more, further preferably 80 % or more.

Here, the average grain size  $\bar{r}$  is defined as the grain size when the product of frequency  $n_i$  of the grains having the grain size  $r_i$  and  $r_i^3$ , namely  $n_i \times r_i^3$  becomes the maximum (effective numeral: 3 ciphers, the smallest cipher numeral of 5 and over being rendered to the next cipher).

Here, the grain size  $r_i$  refers to its diameter in the case of a spherical silver halide grain, while it refers to the diameter when its projected image is calculated as the circular image with the same area in the case of a grain having other shape than spherical shape.

The grain size can be obtained by, for example, photographing said grain by an electron microscope with enlargement to 10,000- to 50,000-fold and measuring the grain diameter of the area when projected on the print (number of grains measured is made indifferently 1,000 or more).

The particularly preferable highly mono-dispersed emulsion of the present invention has a broadness of distribution of 20 % or less, more preferably 15 % or less as defined below:

$$\frac{\text{Standard deviation}}{\text{Average grain size}} \times 100 = \text{Fluctuation coefficient (\%)}$$

Here, the average grain size and the standard deviation are to be determined from  $r_i$  as defined above.

As a method for obtaining a mono-dispersed emulsion, there can be mentioned a method in which a water-soluble silver salt solution and a water-soluble halide solution are added under control of pAg and pH into a gelatin solution containing seed grains according to the double jet method. In determining the addition speed, reference can be made to Japanese Unexamined Patent Publications Nos. 48521/1979 and 49938/1983.

As a method for obtaining a further highly mono-dispersed emulsion, the growth method in the presence of tetrazaindene disclosed in Japanese Unexamined Patent Publication No. 122935/1985 is applicable.

The silver halide emulsion of the present invention can be chemically sensitized in conventional manner.

The silver halide emulsion of the present invention can be optically sensitized to a desired wavelength region by use of a dye known as the sensitizing dye in the field of photography. The sensitizing dye may be used alone, but two or more kinds may be also used in combination.

In the silver halide emulsion, antifoggants, stabilizers, etc. can be added. As the binder for said emulsion, gelatin is advantageously used.

The emulsion layer and other hydrophilic colloid layers can be hardened, and also plasticizers, water-insoluble or difficultly soluble synthetic polymer dispersions (latices) can be contained.

In the emulsion layer of the light-sensitive material for color photography, couplers can be employed.

Further, colored couplers having the effect of color correction, competitive couplers and compounds capable of releasing various fragments through coupling with the oxidized developing agent, namely photographically useful fragments such as development accelerators, bleaching accelerators, developers,

silver halide solvents, color controllers, film hardeners, foggants, antifoggants, chemical sensitizers, spectral sensitizers and desensitizers, can be used.

In the light-sensitive material, auxiliary layers such as filter layer, halation preventiv layer, irradiation preventiv layer, etc., can be provided. In these layers and/or the emulsion layers, a dye which may be flowed out from the light-sensitive material or bleached during developing processing may be also contained.

In the light-sensitive material, formalin scavengers, brightening agents, matting agents, lubricants, image stabilizers, surfactants, color antifoggants, development accelerators, development retarders or bleaching accelerators can be added.

As the support, paper having polyethylene, etc. laminated thereon, polyethyleneterephthalate film, baryta paper, cellulose triacetate, etc. can be used.

For obtaining a dye image by use of the light-sensitive material of the present invention, color photographic processing conventionally known can be practiced after exposure.

15

#### [Examples]

The present invention is described in detail by referring to Examples.

Here, description is made about the present invention by preparing an emulsion of the core/shell type as an embodiment, but it has been also found that the effect of the present invention can be obtained even in other embodiments (an emulsion containing silver halide grains having an average aspect ratio of 11, or an emulsion containing silver halide grains having 3 phases but having no layered (core/shell) structure).

#### (Comparative example 1)

As comparative emulsions, core/shell type emulsions Em-1 and Em-2 were prepared according to the method as disclosed in Japanese Unexamined Patent Publication No. 245151/1986.

30

Table 1

35

Em No.	Grain size ( $\mu\text{m}$ )	Silver iodide content* (mol %)				Volume ratio (%)		
		Core	Intermediate shell	Shell	Whole	Core	Intermediate shell	Shell
Em-1	2.0	40	5	0.3	11.1	22	39	27
Em-2	2.0	50	5	0.3	12.2	22	39	27

40

\* values in formulation

With pAg during core growth as 8.7 and pAg during shell growth as 10.2, pAg during growth of intermediate shell was continuously varied.

45

#### (Comparative example 2)

A core/shell type emulsion Em-3 was prepared according to the method as disclosed in Japanese Unexamined Patent Publication No. 143331/1985.

50

55

Table 2

Em No.	Grain size ( $\mu\text{m}$ )	Silver iodid content* (%)			Volume ratio (%)	
		Core	Shell	Whole	Core	Shell
Em-3	2.05	20	0	10	50	50

\* values in formulation

(Example 1)

In the following, solutions were prepared to prepare the core/shell type emulsion Em-4 of the present invention.

	Ossein gelatin	16.6 g
	Polyisopropylene-polyethylene oxy-	
	disuccinic acid ester sodium salt	
	10 % methanolic solution	10 ml
25	B-1 KBr	1.4 g
	4-Hydroxy-6-meththyl-1,3,3a,7-tetrazaindene	0.5 g
	56 % Acetic acid	175 ml
	28 % Ammonia water	351 ml
	Seed emulsion (mono-dispersed AgBrI	
	emulsion with an average grains size of	
	0.8 $\mu\text{m}$ containing 2.6 mol% of AgI) corresponding	
	to 0.678 mole	
	Added with water to	6 liters
40	Ossein gelatin	25 g
	KBr	228 g



5	B-2	KI	83 g
		4-Hydroxy-6-meththyl-1,3,3a,7-tetrazaindene	0.813 g
		Added with water to	2.5 liters
10		Ossein gelatin	20 g
		KBr	775 g
	B-3	KI	81 g
		4-Hydroxy-6-meththyl-1,3,3a,7-tetrazaindene	1.6 g
		Added with water to	2.0 liters
15		Ossein gelatin	12 g
		KBr	498 g
20	B-4	KI	2.1 g
		4-Hydroxy-6-meththyl-1,3,3a,7-tetrazaindene	0.96 g
		Added with water to	1.2 liters
25		AgNO3	409 g
	A-1	28 % Ammonia water	383 ml
		Added with water to	2410 ml
30		AgNO3	1352 g
	A-2	28 % Ammonia water	1267 ml
35		Added with water to	2273 ml

The B-1 solution at 50 °C was stirred at 1,000 r.p.m. by a stirring device shown in Japanese Unexamined Patent Publication No. 160128/1987. Into this B-1, the solutions B-2 to B-4 and the solutions A-1 to A-2 were added by the double jet method as shown in Table 3. At this time, pH and pAg were controlled by use of an aqueous KBr solution and 56 % acetic acid also as shown in Table 3.

Table 3

Time (minute)	Addition speed of solution (ml/minute)			pAg	pH
	B-3, A-2	B-2, A-1	B-4, A-2		
0.0	6.4	-	-	8.9	8.8
8.5	7.4	-	-	8.9	8.8
23.1	8.2	30.0	-	8.9	8.8
35.8	-	34.1	-	8.9	8.8
51.6	-	41.3	-	8.9	8.8
62.9	-	46.9	-	8.9	8.8
80.2	16.0	55.2	-	8.9	8.8
101.1	20.9	-	-	9.4	8.4
120.8	16.4	-	-	10.0	8.1
144.8	15.1	-	15.1	10.1	7.8
161.8	-	-	15.0	10.1	7.7
180.4	-	-	15.7	10.1	7.5
197.6	-	-	17.6	10.1	7.3

Table 4

Em No.	Grain size ( $\mu$ m)	Silver iodide content* (mol %)				Volume ratio (%)		
		Core	Intermediate shell	Shell	Whole	Core	Intermediate shell	Shell
Em-4	2.0	20	7	0.3	7.4	21	39	27

\* values in formulation

After completion of addition, desalting and water washing were performed in conventional manner. Thus, there was obtained an emulsion Em-4, which was found to have a crystal habit of mainly octahedral and a fluctuation coefficient of 14 % in the grain size distribution.

## Comparative example 3

Em-5 was prepared according to the same procedure as in Example 1 except for using a stirring device as shown in Japanese Unexamined Patent Publication No. 92523/1982.

## Example 2

Em-6 was prepared according to entirely the same procedure as in Example 1 except for using the solution B-5 in place of the solution B-4 in Example 1.

B-5	Ossein gelatin	12 g
	KBr	500 g
	4-Hydroxy-6-methyl-1,3,3a,7-tetrazaindene	0.96 g
	Added with water to	1.2 liters

Table 5

Em No.	Grain size ( $\mu\text{m}$ )	Silver iodide content* (mol %)				Volume ratio (%)		
		Core	Intermediate shell	Shell	Whole	Core	Intermediate shell	Shell
Em-6	2.0	20	7	0	7.3	21	39	27

\* values in formulation

Em-6 was found to have a crystal habit of mainly octahedral and a fluctuation coefficient of 14 % in the grain size distribution.

## Example 3

The states of the contents of silver iodide of the cores of the emulsions and the contents of silver iodide after grain formation in comparative emulsions Em-1, Em-2, Em-3 and Em-5 and the present emulsions Em-4 and Em-6 were examined according to X-ray diffraction. The results are shown in Table 6. Also, the results of measurement of Em-4 after grain formation are shown in Fig. 1.

Table 6

Em No.	Presence of core containing 20 mol % or more of AgI	Number of maximum of diffraction peaks based on X-ray diffraction measurement after grain formation
Em-1	x	1
Em-2	x	1
Em-3	o	2
Em-4	o	3
Em-5	o	1
Em-6	o	3

## Example 4

The comparative emulsions Em-1, Em-2, Em-3 and Em-5 and the present emulsions Em-4 and Em-6 were chemically ripened in the presence of sodium thiosulfate, chloroauric acid and ammonium thiocyanate, divided and added with sensitizing dyes I - V as described below and 4-hydroxy-6-methyl-1,3,3a,7-tetraindene as the stabilizer. By use of this emulsion, the respective layers with the following composition were formed on a triacetylcellulose film support successively from the support side to form a multi-layer light-sensitive color photographic material.

## Sample (standard)

First layer: Halation preventive layer (HC-2) A gelatin layer containing black colloidal silver.

Second layer: Intermediate layer (I.L)  
A gelatin layer

Third layer: Low sensitivity red-sensitive silver halide emulsion layer (RL-2)

A mono-dispersed emulsion comprising AgBr containing 9 mole% of AgI with an average grain size ( $\bar{r}$ ) of 0.80  $\mu\text{m}$  (Emulsion A) and a mono-dispersed emulsion comprising AgBr containing 8 mole% of AgI with an average grain size of 0.4  $\mu\text{m}$

(Emulsion) Silver amount coated 1.7 g/m<sup>2</sup>

Sensitizing dye I  $25 \times 10^{-4}$  mole per mole of silver

Sensitizing dye II  $1.3 \times 10^{-4}$  mole per mole of silver

Cyan coupler (C-1) 0.08 mole per mole of silver

5 Colored cyan coupler (CC-1) 0.004 mole per mole of silver

DIR compound (D-4) 0.0005 mole per mole of silver

Fourth layer : Intermediate layer (I.L.)

A gelatin layer

10 Fifth layer : Low sensitivity green-sensitive silver halide emulsion layer (GL-2)

Emulsion A silver amount coated 1.7 g/m<sup>2</sup>

Emulsion B

Sensitizing dye III  $1.9 \times 10^{-4}$  mole per mole of silver

Sensitizing dye IV  $1.9 \times 10^{-4}$  mole per mole of silver

15 Magenta coupler (M-1) 0.06 mole per mole of silver

Colored magenta coupler (CM-1) 0.012 mole per mole of silver

Sixth layer : Intermediate layer (I.L.)

A gelatin layer

20

Seventh layer: Low sensitivity blue-sensitive silver halide emulsion layer (BL-2)

Emulsion A silver amount coated 1.0 g/m<sup>2</sup>

Sensitizing dye V  $4.2 \times 10^{-4}$  mole per mole of silver

Yellow coupler (Y-1) 0.06 mole per mole of silver

25 DIR compound (D-4) 0.004 mole per mole of silver

Eighth layer: Intermediate layer (I.L.)

A gelatin layer containing emulsified dispersion of D-4

30 Ninth layer : High sensitivity red-sensitive silver halide emulsion layer (RH-2)

Mono-dispersed (distribution 13 %) silver iodobromide emulsion

(Em-1) silver amount coated 2.1 g/m<sup>2</sup> Sensitizing dye I  $1.3 \times 10^{-4}$  mole per mole of silver

Sensitizing dye II  $6.3 \times 10^{-5}$  mole per mole of silver

Cyan coupler (C-2) 0.015 mole per mole of silver

35 Cyan coupler (C-3) 0.015 mole per mole of silver

Colored cyan coupler (CC-3) 0.002 mole per mole of silver

DIR compound (D-4) 0.004 mole per mole of silver

Tenth layer : Intermediate layer (I.L.)

A gelatin layer containing emulsified dispersion of D-4

40 Eleventh layer: High sensitivity green-sensitive silver halide emulsion layer (GH-2)

Mono-dispersed emulsion (Em-1) silver amount coated 2.4 g/m<sup>2</sup>

Sensitizing dye III  $7.0 \times 10^{-5}$  mole per mole of silver

Sensitizing dye IV  $7.0 \times 10^{-5}$  mole per mole of silver

Magenta coupler (M-1) 0.020 mole per mole of silver

45 Colored magenta coupler (CM-1) 0.002 mole per mole of silver

Twelfth layer: Gelatin layer containing emulsified dispersion of D-4

Thirteenth layer : High sensitivity blue-sensitive silver halide emulsion layer (BH-2)

50 Mono-dispersed emulsion (Em-1) silver amount coated 2.1 g/m<sup>2</sup>

Sensitizing dye V  $1.9 \times 10^{-4}$  mole per mole of silver

Yellow coupler (Y-1) 0.08 mole per mole of silver

DIR compound (D-1) 0.0007 mole per mole of silver

55 Fourteenth layer : First protective layer (Pro-3)

Average grain size : 0.07  $\mu$ m

AgI 1 mole% AgBr silver amount coated 0.2 g/m<sup>2</sup>

A gelatin layer containing UV-ray absorbers UV-1, UV-2

Fifteenth layer : Second protective layer (Pro-4)

A gelatin layer containing polymethylmethacrylate grain (diameter: 1.5  $\mu$ m) and formalin scavenger (HS-1)

In the respective layers, in addition to the above compositions, gelatin film hardeners (H-1) and (H-2), and surfactants were added.

The compounds contained in the respective layers of the sample are as follows:

Sensitizing dye I : Anhydro-5,5'-dichloro-9-ethyl-3,3'-di-(3-sulfopropyl)thiacarbocyanine hydroxide

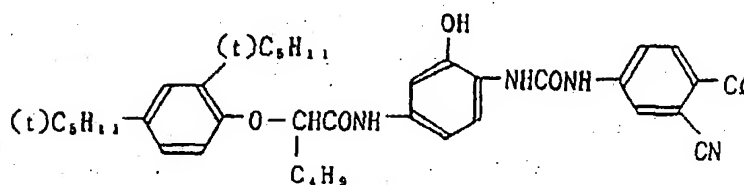
Sensitizing dye II : Anhydro-9-ethyl-3,3'-di-(3-sulfopropyl)-4,5,4',5'-dibenzothiacarbocyanine hydroxide

Sensitizing dye III : Anhydro-5,5'-diphenyl-9-ethyl-3,3'-di-(3-sulfopropyl)oxacarbocyanine hydroxide

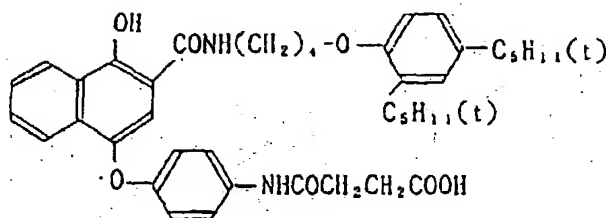
Sensitizing dye IV : Anhydro-9-ethyl-3,3'-di-(3-sulfopropyl)-5,6,5',6'-dibenzooxacarbocyanine hydroxide

Sensitizing dye V : Anhydro-3,3'-di-(3-sulfopropyl)-4,5-benzo-5'-methoxythiacyanine anhydroxide

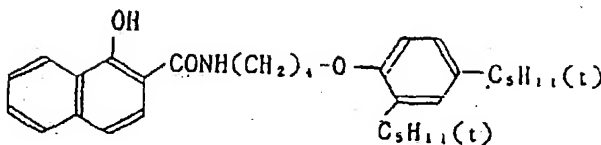
C - 1



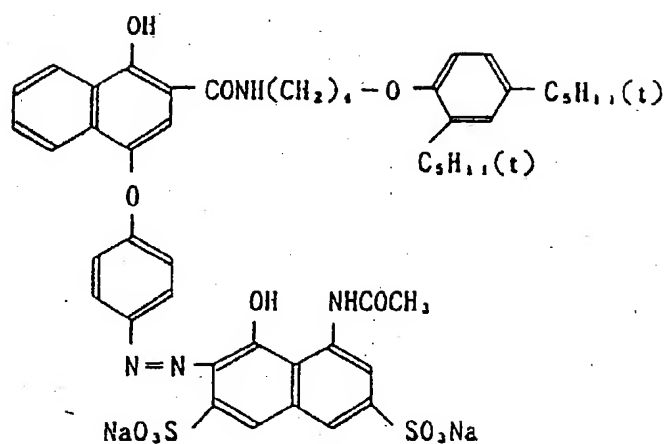
C - 2



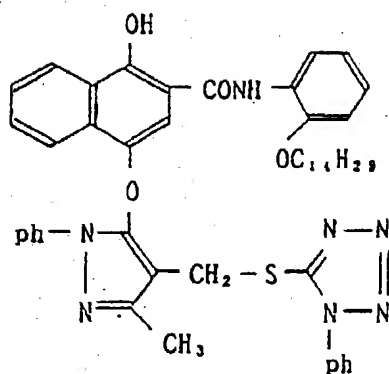
C - 3



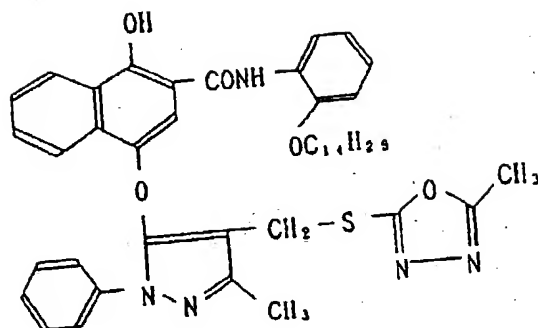
CC - 1



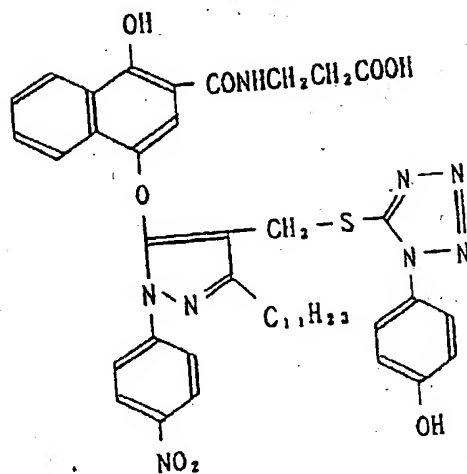
D - 1



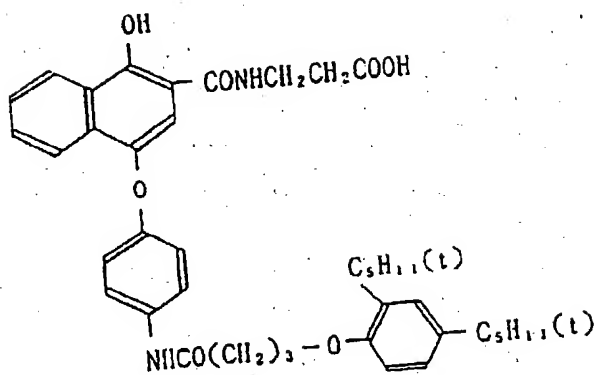
D - 2



D - 3



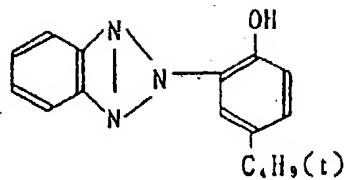
D - 4



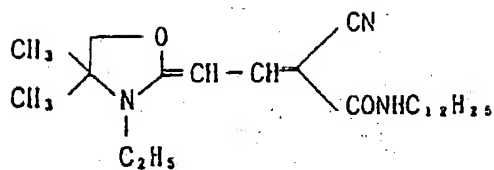




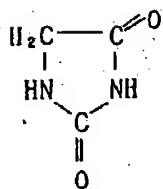
UV - 1



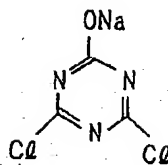
UV - 2



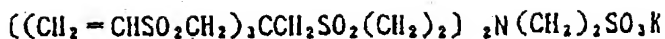
HS - 1



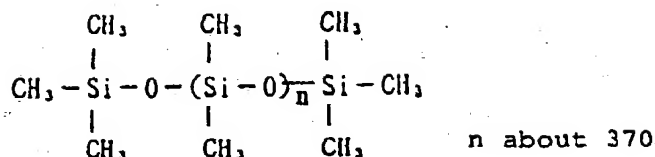
H - 1



H - 2



W A - 1



Next, in the sample 1, in place of the silver halide emulsion Em-1 in the 9th, 11th and 13th layers, Em-2 to Em-6 were used to prepare samples 2 to 6.

The respective samples No. 1 to No. 6 thus prepared were subjected to wedge exposure by use of white light and then the developing processing shown below was conducted.

#### Processing step (38 °C)

Color developing 3 min. 15 sec.  
 Bleaching 6 min. 30 sec.  
 Water washing 3 min. 15 sec.  
 Fixing 6 min. 30 sec.  
 Water washing 3 min. 15 sec.  
 Stabilizing 1 min. 30 sec.  
 Drying

The processing liquors employed in the respective processing steps had the compositions shown below.

#### [Color developer]

4-Amino-3-methyl-N-ethyl-N-(β-hydroxyethyl)aniline-sulfate 4.75 g  
 Anhydrous sodium sulfite 4.25 g  
 Hydroxylamine-1/2 sulfate 2.0 g  
 Anhydrous potassium carbonate 37.5 g  
 Sodium bromide 1.3 g  
 Nitrilotriacetic acid 3 sodium salt(monohydrate) 2.5 g  
 Potassium hydroxide 1.0 g  
 (added with water to one liter)

## [Bleaching solution]

- Iron ammonium ethylenediamin tetraacetate 100 g  
 Diammonium ethyl nediaminetetraacetate 10.0 g  
 5 Ammonium bromid 150.0 g  
 Glacial acetic acid 10.0 ml  
 (added with water to one liter, and adjusted to pH = 6.0 with ammonia water)

## 10 [Fixing solution]

- Ammonium thiosulfate 175.0 g  
 Anhydrous sodium sulfite 8.5 g  
 Sodium metarsulfite 2.3 g  
 15 (added with water to one liter, and adjusted to pH = 6.0 with acetic acid)

## [Stabilizing solution]

- 20 Formalin (37 % aqueous solution) 1.5 ml  
 Konidax® (produced by Konishiroku Photo Industry) 7.5 ml  
 (added with water to one liter)

- 25 For the respective samples obtained, by use of blue light (B), green light (G) and red light (R), relative sensitivity (S) and graininess (RMS) were measured. The results obtained by use of green light are shown in Table 7.

Relative sensitivity (S) is a relative value of reciprocal number of exposure dosage which gives a fog density of 0.1 and shown as the value relative to that of W sensitivity of the sample No. 4 as being 100.

- 30 RMS value was shown in terms of the relative value of the standard deviation of fluctuation of the density value which occurs when scanning is performed at a density higher by +0.3 than the minimum density by use of a microdensitometer having an opened scanning area of 250  $\mu\text{m}^2$ .

RMS value indicates more effectiveness, as its value is smaller.

35 Table-7

Sample No.	Emulsion in 9th, 11th or 13th layer	Relative sensitivity of green sensitive layer	Graininess of green sensitive layer
40 1 (comparative)	Em-1	68	118
2 ( " )	Em-2	55	121
3 ( " )	Em-3	65	113
4 (this invention)	Em-4	100*	100*
5 (comparative)	Em-5	80	105
45 6 (this invention)	Em-6	100	101

As can be seen from Table 7, the samples Nos. 4 and 6 by use of the silver halide emulsion of the present invention can be appreciated to be excellent in both sensitivity and graininess.

- 50 Also, for the red-sensitive layer and the blue-sensitive layer, similar results were obtained.

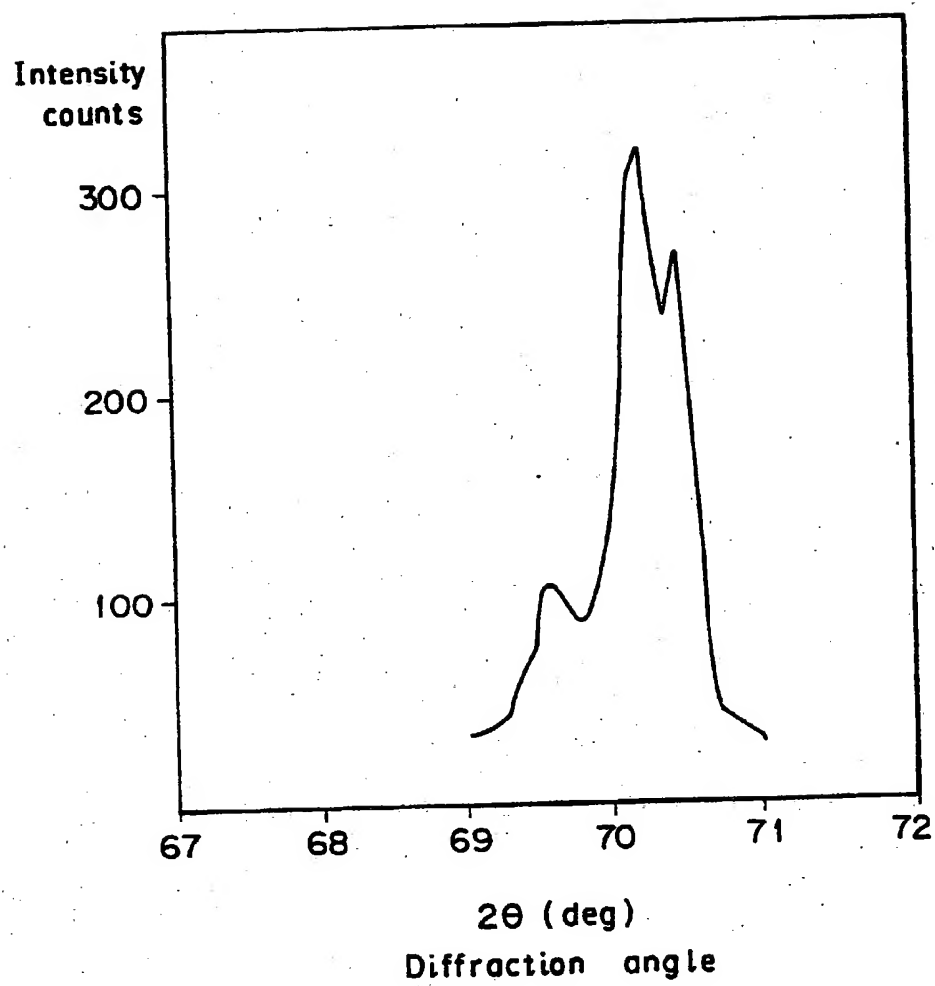
Also, for the product in which the mono-dispersed emulsion in Em-4 was replaced with a poly-dispersed emulsion with a coefficient of fluctuation of 23 %, the effect of the present invention could be obtained.

- Further, an emulsion in which a diffraction intensity of the minimum value sandwiched between the adjacent diffraction peaks is 93 % relative to the weaker one of the adjacent diffraction peaks was prepared and sensitivity and graininess were measured similarly as in Example 4 to give the effect of the present invention.

## Claims

1. A light-sensitive silver halide photographic material having at least one layer of emulsion layer containing an emulsion which is a silver halide emulsion containing silver iodobromide grains having 3 or more phases of silver bromide or silver iodobromide with different compositions, said emulsion having, in the diffraction signal according to powdery X-ray diffraction, 3 or more diffraction maximums based on the diffraction peak corresponding to the maximum iodine content phase, the diffraction peak corresponding to the minimum iodine content phase and one or plural number of diffraction peaks corresponding to the intermediate iodine content phase comprising intermediate compositions between said maximum iodine phase and said minimum iodine phase, and two or more diffraction minimums therebetween.
2. The light-sensitive silver halide photographic material according to Claim 1, wherein diffraction intensity corresponding to a phase which gives the highest intensity among the diffraction maximums is 1 to 50 times relative to the diffraction intensity corresponding to a phase which gives the lowest intensity among the diffraction maximums.
3. The light-sensitive silver halide photographic material according to Claim 1, wherein the diffraction intensity of the minimum value sandwiched between any adjacent two diffraction maximums is 95 % or less of the weaker one of the adjacent two diffraction maximums.
4. The light-sensitive silver halide photographic material according to Claim 1, wherein the relative standard deviation of the distribution of iodine contents between the grains is 50 % or less when measured by the EMPA method.
5. The light-sensitive silver halide photographic material according to Claim 1, wherein the silver iodide content in the maximum iodine content phase is 10 mole% or more.
6. The light-sensitive silver halide photographic material according to Claim 1, wherein the silver iodide content in the minimum iodine content phase is 8 mole% or less.
7. The light-sensitive silver halide photographic material according to Claim 1, wherein the percentage of the minimum iodine content phase in the whole grains is 10 to 80 % by volume.
8. The light-sensitive silver halide photographic material according to Claim 1, wherein the percentage of the maximum iodine content phase in the whole grains is 10 to 80 % by volume.
9. The light-sensitive silver halide photographic material according to Claim 1, wherein the silver iodide content in the intermediate iodine phase is 3 mole% or more.
10. The light-sensitive silver halide photographic material according to Claim 1, wherein the percentage of intermediate iodine content phase in the whole grains is 5 to 80 % by volume.
11. The light-sensitive silver halide photographic material according to Claim 1, wherein the maximum iodine content phase exists as the internal nucleus internally of the grain, the minimum iodine content phase exists as the shell outside of the internal nucleus and one or a plural number of the intermediate iodine content phases exist as the intermediate layer between the internal nucleus and the shell or inside of the internal nucleus, or in both thereof.
12. The light-sensitive silver halide photographic material according to Claim 1, wherein the silver halide emulsion is a silver iodobromide, with an average silver iodide content of 5 mol% or more.
13. The light-sensitive silver halide photographic material according to Claim 1, wherein the silver halide emulsions are a core/shell type emulsion.
14. The light-sensitive silver halide photographic material according to Claim 13, wherein the silver halide emulsions are prepared according to a method in which the seed emulsion is grown according to the double jet method, while controlling pAg and pH.
15. The light-sensitive silver halide photographic material according to Claim 14, wherein the pAg during growth of core is 6 to 10, while the pAg during growth of shell is 9 to 11.
16. The light-sensitive silver halide photographic material according to Claim 14, wherein the feeding of the reaction solutions in said double jet method is performed according to a feeding method in which plurality of feeding nozzles are provided for one reaction solution in such a manner that the feeding nozzles are immersed in the mother liquid in reaction tank and located adjacent to the mother liquid inlet of the stirrer provided in the tank.
17. The light-sensitive silver halide photographic material according to Claim 1, wherein the size of the silver halide grain in the emulsion is 0.05 to 30  $\mu\text{m}$ .
18. The light-sensitive silver halide photographic material according to Claim 1, wherein the silver halide emulsion is a mono-dispersed one in which the weight of silver halide grains having a grain size included within the range of  $\pm 20$  % from an average grain size  $\bar{r}$  as the center corresponds to 60 % or more of the weight of all the silver halide grains.

FIG. 1



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71 Applicant: **KONICA CORPORATION**  
No. 26-2, Nishi-Shinjuku 1-chome Shinjuku-ku  
Tokyo 106 (JP)

72 Inventor: **Mochizuki, Yoshiharu**  
c/o Konica Corporation 1, Sakuramachi  
Hino-shi Tokyo (JP)

**Ishikawa, Sadayasu**  
c/o Konica Corporation 1, Sakuramachi  
Hino-shi Tokyo (JP)

**Yagi, Toshihiko**  
c/o Konica Corporation 1, Sakuramachi  
Hino-shi Tokyo (JP)

**Inoue, Masamitsu**  
c/o Konica Corporation 1, Sakuramachi  
Hino-shi Tokyo (JP)

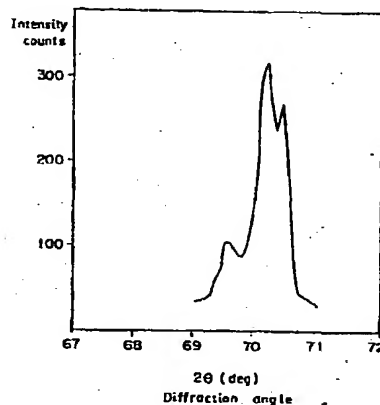
79 Representative: **Wood, Anthony Charles et al**  
Urquhart-Dykes & Lord 91 Wimpole Street  
London W1M 8AH (GB)

54 High sensitivity, high graininess light-sensitive silver halide photographic material.

57 A light-sensitive silver halide photographic material having at least one layer of emulsion layer containing an emulsion which is a silver halide emulsion containing silver iodobromide grains having 3 or more phases of silver bromide or silver iodobromide with different compositions, the emulsion having, in the diffraction signal according to powdery X-ray diffraction, 3 or more diffraction maximums based on the diffraction peak corresponding to the maximum iodine content phase, the diffraction peak corresponding to the minimum iodine content phase and one or plural number of diffraction peaks corresponding to the intermediate iodine content phase comprising intermediate compositions between the maximum iodine content phase and the minimum iodine content phase, and two or more diffraction minimums therebetween.

According to the present invention, there can be obtained a light-sensitive silver halide photographic material with high sensitivity and high graininess.

FIG. 1





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	DE-A-3 310 609 (MINNESOTA MINING AND MANUFACTURING CO.) * Claims; page 9, line 28 - page 10, line 22; page 16, line 30 - page 17, line 30 *	1-18	G 03 C 1/02
X,D	JOURNAL OF PHOTOGRAPHIC SCIENCE, vol. 10, pages 129-134, Royal Photographic Society, London, GB; H. HIRSCH: "Photographic emulsion grains with cores. Part 1. Evidence for the presence of cores" * Page 132, right-hand column, lines 5-12; figure 3 *	1-3,5-13	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			G 03 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16-03-1989	Examiner BUSCHA A.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	